THE INFLUENCE OF REACTANT CONSUMPTION ON THE CRITICAL CONDITIONS FOR HOMOGENEOUS THERMAL EXPLOSIONS

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The spatially homogeneous model of a high activation energy thermal explosion is studied when the heat loss parameter a is close to the classically-defined critical value $a = e$. Asymptotic solutions are developed which describe the time-history of the temperature and reactant depletion. It is shown that there is a critical time period, large with respect to the characteristic conduction time, in which the temperature variation is described by a Riccati equation. The solution properties of this nonlinear equation permit one to define a value of $\Delta = a - e$ which separates subsequent subcritical and supercritical behaviour.

1. Introduction

THE study of the spatially homogeneous model of a thermal explosion in a premixed gas system has been of continuous interest since the work of Semenov (**1**). Recent reviews of this subject and related matters can be found in Gray and Lee (**2**) and Hlavacek (**3**). Particular emphasis has been placed on developing the conditions for criticality (**4** to **6**); the parameter boundary separating systems which explode, in the sense of rapid, large temperature increases, from those which merely fizzle a bit. The history of this effort has been described by Gray and Sherrington (**7**) and hence will not be repeated here. Until recently, one could conclude that somewhat *ad hoc* techniques prevented the development of definitive criticality criteria.

Gray and Sherrington (**7**) showed that Liapunov stability techniques could be applied to an approximate form of the complete thermal explosion equations to find criticality criteria. The approximation is based ostensibly on the condition that the heat of reaction is large compared to the initial thermal energy in the system. It is shown that the classically defined criticality criteria, usually obtained from ignition-type analysis in which reactant consumption is absent, are implied by the more complete equations including reactant consumption. Unfortunately, the analysis is based on a set of approximate equations which cannot be derived rationally for the limit of large heat-of-reaction. The use of the exponential approximation in equations (1) and (2) of (**7**) implies, at least formally, that the activation energy is large as well. Hence, the results cannot be considered definitive in so far as the complete thermal explosion equations are concerned.

More recently Kassoy and co-workers (**8** to **11**) have developed asymptotic expansion techniques which can be used to develop complete descriptions of the spatially homogeneous thermal explosion for the limit of high activation energy. In (**9**) and (**10**), the time-history of the temperature and reactant consumption is given for the adiabatic system. The solution describes not just the classical ignition period but the rapid reaction process when the temperature rises significantly and most of the reactant is consumed. The subcritical explosion is dealt with in (**8**). The analysis, including complete reactant consumption, is carried out for values of the heat-loss parameter $a > e$. The temperature is shown to rise during a time period measured by the conduction time scale and then decline over a much longer time. During the latter period, most of the reactant consumption occurs. In the limit $a \to e^+$ the asymptotic expansion procedure fails, suggesting that critical behaviour is being approached. In the case $a < e$ the classical theory predicts a supercritical explosion. This case has been described from initiation to completion in (**11**). The results of that analysis once again confirm that even when reactant depletion is considered a true thermal explosion occurs when $a < e$.

In the present work the nearly critical explosion, when $a \to e$, is examined in detail. Solutions are developed in terms of matched asymptotic expansions defined for the limit of large activation energy. These solutions describe the time-history of the temperature variation and reactant depletion when the heat-loss parameter is defined by $a = e + \Delta$, $\Delta \ll 1$. The functional dependence of Δ on the activation energy is found in the process of analysis. The time-dependence properties of the solutions are used to define a precise criticality criterion in terms of a specific value of $\Delta \equiv \Delta_{crit}$. It is shown that when $\Delta \leq \Delta_{crit}$, a delayed supercritical (explosion) event always occurs. For any larger value of the heat loss parameter, when $\Delta > \Delta_{crit}$, the process always evolves into the subcritical mode. In this sense one can discriminate, in a precise fashion, between a system which will definitely explode and one which will ultimately fizzle a bit.

2. Mathematical model

The nondimensional describing system for a spatially homogeneous thermal explosion associated with an irreversible one-step reaction and a linear heat sink (**14**) can be written in the form

$$T'(\tau)=\epsilon y^n \exp\left\{\frac{1}{\epsilon}\frac{(T-1)}{T}\right\}-a(T-1), \qquad T(0)=1, \tag{2.1}$$

$$y'(\tau)=-\epsilon\gamma y^n \exp\left\{\frac{1}{\epsilon}\frac{(T-1)}{T}\right\}, \qquad y(0)=1. \tag{2.2}$$

The details of the nondimensionalization are described in (**8**). For completeness it is noted that T is the temperature, y is the reactant concentration, n is the overall reaction order, and a is the heat-loss parameter. The time τ is measured with respect to the characteristic conduction time of the system. The quantity γ is the ratio of the initial thermal energy in the system to the potential reaction energy to be released during the entire chemical process. This is an $O(1)$-quantity with respect to the parameter ϵ which represents the ratio of the thermal energy in the system to the activation energy of the one-step reaction. It is assumed that $\epsilon \ll 1$. A solution for (1) and (2) is to be found for the limit $\epsilon \to 0$ when $a=e+\Delta(\epsilon)$, where $\Delta(\epsilon)\ll 1$. In particular, an explicit formula for $\Delta(\epsilon)$ is to be found which can be used to discriminate between sub- and supercritical explosions. Thus when $a-e>\Delta(\epsilon)$ the former prevails, while if $a-e<\Delta(\epsilon)$, a truly explosive event results.

It is to be noted that the limit process used here, $\epsilon\to 0$, $\gamma=O(1)$, differs from that used in (**7**) and by Gray (**12, 13**)($\gamma\to 0$, $\epsilon=O(1)$). The former permits one to develop a rational extension of the classical theory as outlined by Frank-Kamenetskii (**14**) and discussed in references (**8** to **11**). On the other hand, the latter approximation lacks this feature as discussed by Gray himself (**12, 13**). It should also be noted that parametric sensitivity of solutions for (2.1) and (2.2) occurs only in the limit $\epsilon\gamma\to 0$, for $\epsilon<\frac{1}{4}$, as can be derived from the analysis by Gray (**12, 13**). However, the precipitous rise in temperature (thermal runaway) associated with thermal explosions will occur only when both $\epsilon\gamma$ and ϵ are small compared to unity.

3. The subcritical solution for $a \to e$

Preliminary to the investigation of the criticality problem it is useful to consider some aspects of the subcritical solution in (**8**) when $a\to e^+$. In particular, an estimate of the magnitude of $\Delta(\epsilon)=a-e$ is sought. Equations (14) and (15) of (**8**) which describe the asymptotic behaviour of the temperature and reactant during the analogue of the ignition period, can be written as

$$T(\tau\to\infty)\sim 1+\epsilon[\theta_M - K\exp\{-a(1-\theta_M)\tau\}+\dots]+ \\ +\epsilon^2\left\{\frac{-n\gamma a\theta_M^2}{(1-\theta_M)}\tau+O(1)\right\}+O(\epsilon^3), \tag{3.1}$$

$$y(\tau\to\infty)\sim 1-\epsilon\gamma[a\theta_M\tau+\ln\{Ka(1-\theta_M)\}+o(1)]+O(\epsilon^2), \tag{3.2}$$

where

$$\theta_M^{-1} \exp \theta_M = a, \qquad K = O(1). \tag{3.3}$$

The quantity θ_M represents the maximum temperature disturbance associated with a prescribed value of the heat-loss parameter a. When $a \to e^+$ (3.3) implies that $\theta_M \to 1^-$. Hence it is convenient to consider the character of (3.1) when $\alpha(\epsilon) = 1 - \theta_M \ll 1$:

$$T(\tau \to \infty) \sim 1 + \epsilon - \epsilon\alpha - K\epsilon e^{-\epsilon\alpha\tau} + \epsilon^2\left\{\frac{-n\gamma e\tau}{\alpha} + O(1)\right\} + O(\epsilon^3). \tag{3.4}$$

The first two terms represent the critical temperature defined by classical theory as discussed in (**8**), while the remaining terms describe deviations. For any given large τ, the fifth term in (3.4), arising from an $O(\epsilon^2)$-effect in (3.1) will be as large as the third term, arising from an $O(\epsilon)$-effect, if $\alpha^2 = O(\epsilon\tau)$. Furthermore, the exponential decay term in (3.4) will be altered in character when $\alpha = O(\tau^{-1})$. These two estimates can be combined to give $\alpha = O(\epsilon^{\frac{1}{3}})$ and $\tau = O(\epsilon^{-\frac{1}{3}})$, and from (3.3) we find that

$$a \sim e\{1 + O(\epsilon^{\frac{2}{3}})\}, \tag{3.5}$$

which provides a first-order estimate for $\Delta(\epsilon)$. These results, combined with (3.2) and (3.4), suggest further that there is a time scale $\tau = O(\epsilon^{-\frac{1}{3}})$ in which

$$T \sim 1 + \epsilon - O(\epsilon^{\frac{4}{3}}), \qquad y \sim 1 - O(\epsilon^{\frac{2}{3}}). \tag{3.6}$$

Each of these inferences, which are suggestive rather than definitive, will be verified by the full calculation which follows.

4. Initiation phase

The forms of (2.1) and (2.2) suggest that a distinguished limit can be obtained if $T - 1 = O(\epsilon)$, $1 - y = O(\epsilon)$ for $\epsilon \to 0$, τ fixed. This results in an inherent balance of all the terms and hence the representative physical effects, in the equations. It is assumed that the solutions can be expressed as limit-process expansions (**19**)

$$T \sim 1 + \epsilon \sum_{m=1} \mu_m(\epsilon)\theta_m(\tau), \qquad y \sim 1 - \epsilon \sum_{m=1} \nu_m(\epsilon) y_m(\tau), \tag{4.1a,b}$$

where $\mu_1 = \nu_1 = 1$ for the limit $\epsilon \to 0$. The asymptotic sequences μ_m and ν_m can be found only after (4.1a, b) and an appropriate expansion for the heat-loss parameter a are used in (2.1) and (2.2) and the limit process is applied. Equation (3.5) suggests that

$$a \sim e\left\{1 + \sum_{m=1} a_m \epsilon^{(m+1)/3}\right\}, \qquad a_m = O(1), \tag{4.2}$$

where the values of a_m that can be used to discriminate between sub- and supercritical explosions are to be found. It follows that the describing systems for $m=1,2$ are

$$\theta_1' = e^{\theta_1} - e\theta_1, \qquad y_1' = \gamma e^{\theta_1}, \qquad \theta_1(0) = y_1(0) = 0, \tag{4.3a, b}$$

$$\left.\begin{array}{l} \theta_2' = \theta_2 e^{\theta_1} - e(\theta_2 + a_1\theta_1), \qquad y_2' = \gamma e^{\theta_1}\theta_2, \\ \mu_2 = \nu_2 = \epsilon^{\frac{2}{3}}, \qquad \theta_2(0) = y_2(0) = 0. \end{array}\right\} \tag{4.4a,b,c}$$

The solution of (4.3), written in quadrature form, is

$$\tau = \int_0^{\theta_1} \frac{dx}{e^x - ex}, \qquad y_1 = \gamma \int_0^{\theta_1} \frac{e^x\, dx}{e^x - ex}, \tag{4.5a, b}$$

which exhibits a singularity when $\tau \to \infty$, $\theta_1 \to 1^-$. An asymptotic analysis then leads to the results

$$\theta_1(\tau \to \infty) \sim 1 - \frac{2}{e\tau} + O(\tau^{-2}), \tag{4.6}$$

$$y_1(\tau \to \infty) \sim \gamma\{e\tau - 2 \ln \tau + O(1)\}. \tag{4.7}$$

Thus it may be inferred from (4.1) and (4.6) that the temperature is approaching the critical value $1+\epsilon$ in an algebraic fashion (compare with the exponential decay in (3.1)) and the reactant consumption is becoming increasingly large as $\tau \to \infty$. This may be contrasted with the supercritical explosion ignition period described in (**9** to **11**), where a thermal runaway and the concomitant large depletion of reactant begins to occur when $\tau \approx \tau_0 = O(1)$.

The solution to (4.4) in quadrature form is given by

$$\theta_2(\tau) = -a_1 e\theta_1'(\tau) \int_0^{\theta_1} \frac{x\, dx}{(e^x - ex)^2}, \tag{4.8a}$$

$$y_2(\tau) = \gamma \int_0^{\theta_1} \frac{e^x \theta_2(x)\, dx}{e^x - ex}. \tag{4.8b}$$

The asymptotic behaviour of these functions is found to be

$$\theta_2(\tau \to \infty) \sim -\tfrac{1}{3} a_1 e\tau + O(1), \tag{4.9}$$

$$y_2(\tau \to \infty) \sim -\tfrac{1}{6} a_1 e^2 \gamma \tau^2. \tag{4.10}$$

If (4.1), (4.6), (4.7), (4.9) and (4.10) are combined, then one notes that there are several possible indications of a nonuniformity for $\tau \to \infty$. The growth rate of (4.7) in the reactant expansion suggests that the singularity occurs when $\tau = O(\epsilon^{-1})$. However, subsequent use of this estimate in (4.10) implies a reactant variation greater than $O(1)$ which is physically unacceptable. An alternative is to consider a balance of the first decay term in (4.6) with the growth rate in (4.9). This implies that the $O(\epsilon)$-deviation of the temperature from the critical value $1+\epsilon$ is of the same magnitude as the $O(\epsilon^{\frac{5}{3}})$-correction when $\tau = O(\epsilon^{-\frac{1}{3}})$. In this time regime, $T - (1+\epsilon) = O(\epsilon^{\frac{4}{3}})$

and $y-1=O(\epsilon^{\frac{2}{3}})$. These results are equivalent to the estimates given in (3.6) which were found from the subcritical solution in the limit $a \to e^{+}$. Finally, one could balance the growth rates in (4.7) and (4.10) to obtain $\tau = O(\epsilon^{-\frac{2}{3}})$. However, subsequent usage of this estimate in the temperature expansion would imply a critical temperature value of $1+C\epsilon$, where $C \neq 1$. This result is unacceptable because the critical value must be $1+\epsilon$ to the $O(\epsilon)$-approximation (**8**). It is then concluded that the second alternative is appropriate.

These results suggest that when the heat-loss parameter is close to the critical value the ignition-type of reaction phenomena occurs during a time-period which is long compared with the conduction time. The temperature rises slightly and only a small amount of reactant is consumed. There seems to be neither an indication of incipient explosion nor of irrevocable decline of thermal activity. Hence one must proceed further in time to determine the ultimate outcome of the reaction event.

5. The critical regime

The nonuniformity in the initiation-process expansions suggests that the appropriate scalings in the regime of critical behaviour are

$$s=\epsilon^{\frac{1}{3}}\tau, \qquad T=1+\epsilon+\epsilon^{\frac{4}{3}}\phi, \qquad y=1+\epsilon^{\frac{2}{3}}Y. \tag{5.1a,b,c}$$

To find the form of the limit process expansions for ϕ and Y the matching conditions for the temperature and concentration must be constructed from (4.1), (4.6), (4.7), (4.9), (4.10) and (5.1a). These are found to be

$$T(s\to 0)\sim 1+\epsilon-\epsilon^{\frac{4}{3}}\left\{\frac{2}{es}+\frac{1}{3}a_1 es+O(s^2)\right\}+O(\epsilon^{\frac{5}{3}}), \tag{5.2}$$

$$y(s\to 0)\sim 1-\epsilon^{\frac{2}{3}}\gamma es-\tfrac{2}{3}(\epsilon\ln\epsilon)\gamma+\epsilon\{2\ln s+O(1)\}+O(\epsilon^{\frac{4}{3}}). \tag{5.3}$$

It may be inferred that

$$Y\sim Y_0-(\epsilon^{\frac{1}{3}}\ln\epsilon)Y_{11}+\epsilon^{\frac{1}{3}}Y_1+O(\epsilon^{\frac{2}{3}}), \qquad \phi\sim\phi_0+O(\epsilon^{\frac{1}{3}}) \tag{5.4a,b}$$

are valid for the limit process $\epsilon\to 0$, s fixed.

If (5.1) and (5.4) are substituted into (2.1) and (2.2) and the limit process is applied, then we obtain the systems

$$\phi_0'(s)=e(\tfrac{1}{2}\phi_0^2+nY_0-a_1), \qquad Y_0'(s)=-\gamma e, \tag{5.5a,b}$$

$$Y_{11}'(s)=0, \qquad Y_1'(s)=-\gamma e\phi_0, \tag{5.5c,d}$$

which are subject to the matching conditions in (5.2) and (5.3).

It is evident immediately that

$$Y_0=-\gamma es, \qquad Y_{11}=\tfrac{2}{3}\gamma. \tag{5.6a,b}$$

Hence a Riccati equation for ϕ_0 is found from (5.5a) and (5.6a):

$$\phi_0'(s)=e(-\gamma nes-a_1+\tfrac{1}{2}\phi_0^2), \tag{5.7}$$

subject to the condition

$$\phi_0(s \to 0) \sim -\frac{2}{es} - \frac{1}{3} a_1 es + O(s^2). \tag{5.8}$$

Eq. (5.7) is similar in content to (15i) of Thomas (**4**). It should be noted however that Thomas' derivation depends upon two *ad hoc* approximations. These include; (i) the Gray and Harper (**15**) quadratic temperature approximation for the Arrhenius exponential and (ii) the approximation of the reactant consumption equation through the use of a mean value for the quadratic temperature approximation. Nevertheless, the present rational asymptotic analysis shows that the derivation by Thomas was essentially sound although the coefficients of the quadratic approximation are erroneous. This occurs because the coefficients were chosen by assuming that the quadratic approximation should have the same value and slope as the full exponential at $T = 1 + \epsilon$, and give the same rate at $T = 1$. The asymptotic analysis in effect shows that the approximation should be based on having equal values of the function, the slope and the curvature of the two quantities when $T = 1 + \epsilon$.

As is the case in many weakly nonlinear stability problems, the stability criteria are to be determined from the properties of the Landau-type equation (5.7).

The Riccati equation (5.7) can be transformed into an Airy equation by means of a standard transformation (**16**). It follows that the solution can be written in the alternative forms

$$\phi_0 = -\Gamma\left\{\frac{A_1'(z) + KB_1'(z)}{A_1(z) + KB_1(z)}\right\} = -\Gamma\left\{\frac{kA_1'(z) + B_1'(z)}{kA_1(z) + B_1(z)}\right\}, \tag{5.9a,b}$$

$$\Gamma = (4\gamma n)^{\frac{1}{3}}, \qquad z = \hat{a}_1 + \hat{\gamma} s, \tag{5.9c,d}$$

$$\hat{a}_1 = 2^{-\frac{1}{3}} a_1 (\gamma n)^{-\frac{2}{3}}, \qquad \hat{\gamma} = 2^{-\frac{1}{3}} e (\gamma n)^{\frac{1}{3}}. \tag{5.9e,f}$$

Here $A_1(z)$ and $B_1(z)$ are linearly independent Airy functions and primes denote differentiation with respect to z. The integration constants K and k are found by using (5.9) in the z-variable analogue of (5.8),

$$\phi_0(z \to \hat{a}_1) \sim -\Gamma/(z - \hat{a}_1) - \tfrac{1}{3}(a_1 e/\hat{\gamma})(z - \hat{a}_1) + \ldots. \tag{5.10}$$

It follows that

$$K = -A_1(\hat{a}_1)/B_1(\hat{a}_1), \qquad B_1(\hat{a}_1) \neq 0, \tag{5.11}$$

or

$$k = 0, \qquad B_1(\hat{a}_1) = 0, \qquad A_1(\hat{a}_1) \neq 0. \tag{5.12}$$

The solution found from (5.9), (5.11) and (5.12) must now be carefully examined to determine the properties of ϕ_0 as a function of the parameter $\hat{a}_1$. It is clear from (5.1b) that a singularity represented by $\phi_0 \to \infty$ would imply a slightly supercritical event to follow, while the form $\phi_0 \to -\infty$ would suggest a subcritical process. Thus we seek the value of $\hat{a}_1$ which provides a boundary between the two extremes.

Case (*a*)

$$K=0, \qquad \phi_0=-\Gamma A_1'(z)/A_1(z).$$

Equation (5.11) implies that this case occurs when $A_1(\hat{a}_1)=0$ which is satisfied by a discrete set of $\hat{a}_1 \equiv \hat{a}_{1i}$ (**17**), the first few of which are $\hat{a}_{11}=-2{\cdot}338\ldots$, $\hat{a}_{12}=-4{\cdot}0879\ldots$. If we use $\hat{a}_{11}$, then the properties of $A_1(z)$ (**17**) are such that $\phi_0(z)$ is a monotonically increasing function shown qualitatively in Fig. 1 which becomes singular in the sense of

$$\phi_0(\hat{a}_{11}; z \to \infty) \sim \Gamma z^{\frac{1}{2}}\{1+O(z^{-\frac{3}{2}})\}. \tag{5.13}$$

This implies a further growth in the temperature. It should be noted from (5.9d) that this asymptotic form implies that $s \to \infty$. The use of the more negative $\hat{a}_{12}$ leads to the conclusion that $\phi_0(z)$ is a monotonically increasing function which becomes singular when $z \to \hat{a}_{11}^-$ as shown in Fig. 1. Similarly, the use of higher-order $\hat{a}_{1i}$ leads to singularities in $\phi_0(z)$ at the adjacent $\hat{a}_{1(i-1)}$. Translated into the s-plane time scale, this means that as the order of $\hat{a}_{1i}$ is increased, and hence from (4.2) the heat loss is reduced, the slightly supercritical phenomenon occurs earlier in time.

Case (*b*)

$$\hat{a}_1 > \hat{a}_{11} = -2{\cdot}338\ldots.$$

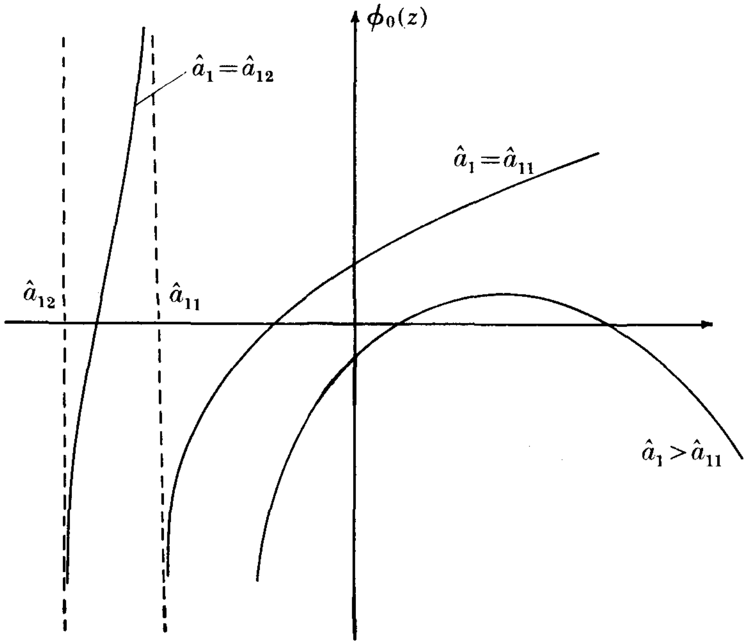

FIG. 1 The qualitative behaviour of the $\phi_0(z)$ function for three values of $\hat{a}_1$.

For this case two subranges are required because $B_1=0$ at $\hat{a}_1 \equiv \hat{a}_1^* = 1{\cdot}17371$. Thus for $\hat{a}_{11} < \hat{a}_1 < \hat{a}_1^*$ it is found that $K>0$ and there are no singularities in the denominator of (5.9a) for $z > \hat{a}_1$. When $z \to \infty$ the $B_1(z)$-contributions dominate and

$$\phi_0(z \to \infty) \sim -\Gamma z^{\frac{1}{2}}\{1 + O(z^{-\frac{3}{2}})\}. \tag{5.14}$$

The general qualitative functional behaviour is shown in Fig. 1. The negative sign in (5.14) implies that this case is slightly subcritical.

For $\hat{a}_1 = \hat{a}_1^*$ (5.9b) is used directly with $k=0$. Here the nonmonotonic variation in $\phi_0(z)$ is quite apparent from the behaviour of $B_1(z)$ alone. It is qualitatively identical to that found in the preceding subrange.

As $\hat{a}_1$ is made less negative, thereby increasing the system heat loss, it is obvious that the function $\phi_0(z)$ should continue to exhibit the subcritical behaviour found previously. Thus for $\hat{a}_1 > \hat{a}_1^*$ one finds $K<0$ and no further singularities in the denominator of (5.9a). Beyond a certain finite value of z the solution describes an irrevocable decline in temperature. Thus we may conclude that for $\hat{a}_1 > \hat{a}_{11}$ there is sufficient heat loss to preclude the possibility of a subsequent supercritical explosion.

Case (*c*)

$$\hat{a}_{1(i+1)} < \hat{a}_1 < \hat{a}_{1i} \leqslant -2{\cdot}338\ \ldots .$$

In each of these ranges two categories of solution need to be considered. For the case when $B_1(\hat{a}_1)=0$, the solution is represented by (5.9b) with $k=0$. The properties of $B_1(z)$ imply that as z increases away from the particular $\hat{a}_1$ (the minimum value of z) another zero of B_1 will be encountered. It is always the case that ϕ_0 becomes indefinitely large and positive at this intersection, implying a subsequent supercritical event. In the general case $B_1(\hat{a}_1) \neq 0$ it can be shown from the Airy-function properties that there is always a finite value of $z > \hat{a}_1$ at which the denominator of (5.9a) becomes singular such that ϕ_0 is large and positive.

It may now be concluded that to $O(\epsilon^{\frac{2}{3}})$ the value of the heat-loss parameter dividing supercritical from subcritical events is defined by

$$a \sim e\{1 - 2{\cdot}946(\gamma n\epsilon)^{\frac{2}{3}} + o(\epsilon)\}. \tag{5.15}$$

Thomas (**4**) found a very similar result where the coefficient in the second term is 2·85. The difference is caused by the use of the two *ad hoc* approximations mentioned earlier in this section.

Gray and Lee (**2**) have suggested that the form

$$a = e\{1 + 2{\cdot}946(\gamma n\epsilon)^{\frac{2}{3}}\}^{-1},$$

which is equivalent to (5.15) for small $\epsilon\gamma$, will provide accurate results for larger values of $\epsilon\gamma$.

6. Critical régime asymptotics and beyond

The singular behaviour of solutions in the critical régime can be used to estimate the nature of nonuniformities and subsequent solution behaviour.

For the subcritical case $\hat{a}_1 > -2{\cdot}338\ldots$ the asymptotic form in (5.14) can be combined with (5.1b, c) and (5.9) to show that

$$T(s \to \infty) \sim 1 + \epsilon + \epsilon^{\frac{4}{3}}\{-(2\gamma ne)^{\frac{1}{2}}s^{\frac{1}{2}} + O(s^{-\frac{1}{2}})\} + O(\epsilon^{\frac{5}{3}}), \tag{6.1}$$

$$y(s \to \infty) \sim 1 + \epsilon^{\frac{2}{3}}(-\gamma es) + O(\epsilon \ln \epsilon). \tag{6.2}$$

These results can be interpreted to mean that when $s = O(\epsilon^{-\frac{2}{3}})$ there is a nonuniformity. This occurs when $\tau = O(1/\epsilon)$, $T = 1 + O(\epsilon)$ with $\Delta T = O(\epsilon)$ and $y = O(1)$ with $\Delta y = O(1)$, where the Δ-symbol refers to variations in the quantity. If we use the scalings $T = 1 + \epsilon\hat{\theta}$, $y = \hat{y}$, and $\tau = r/\epsilon$ in (2.1), (2.2), (6.1) and (6.2) and apply the limit $\epsilon \to 0$, r fixed, then the lowest-order describing system is

$$\hat{y}_0^n e^{\theta_0} = e\hat{\theta}_0, \qquad \hat{y}_0'(r) = -\gamma \hat{y}_0^n e^{\hat{\theta}_0}, \tag{6.3a,b}$$

$$\hat{\theta}_0(r \to 0) \sim 1 - (2\gamma ne)^{\frac{1}{2}} r^{\frac{1}{2}} + \ldots\ , \tag{6.4a}$$

$$\hat{y}_0(r \to 0) \sim 1 - \gamma er + \ldots\ . \tag{6.4b}$$

This system is very similar to that found for the fully subcritical explosion in (**8**). It is known to describe monotonic temperature decay and reactant consumption.

When $\hat{a}_1 = -2{\cdot}3381$ the asymptotic behaviour of $\phi_0(z)$ is given by (5.13). It follows that

$$T(s \to \infty) \sim 1 + \epsilon + \epsilon^{\frac{4}{3}}\{(2\gamma ne)^{\frac{1}{2}}s^{\frac{1}{2}} + O(s^{-\frac{1}{2}})\} + O(\epsilon^{\frac{5}{3}}). \tag{6.5}$$

Equation (6.2) continues to be valid. Formally the singularity is as described in the previous case. As a result the quoted scalings remain valid. The lowest-order describing system includes (6.3a, b) and (6.4b). However (6.4a) is replaced by

$$\hat{\theta}_0(r \to 0) \sim 1 + (2\gamma ne)^{\frac{1}{2}} r^{\frac{1}{2}} + \ldots. \tag{6.6}$$

Now (6.3a, b) can be combined to produce an equation for the temperature variation

$$\theta_0' = \frac{\gamma ne^{(n-1)/n}\hat{\theta}_0^{(2n-1)/n}\exp(\hat{\theta}_0/n)}{(\hat{\theta}_0 - 1)} \tag{6.7}$$

From (6.5) we see that the denominator is always positive so that $\hat{\theta}_0' > 0$. Furthermore increases in $\hat{\theta}_0$ always lead to further increases in $\hat{\theta}_0$ which implies that (6.7) describes an explosive event. The formal solution, in quadrature form,

$$\gamma ne^{(n-1)/n} r = \int_1^{\hat{\theta}_0} \frac{(x-1)e^{-x/n}\,dx}{x^{(2n-1)/n}}, \tag{6.8}$$

has the property that

$$\hat{\theta}_0(r \to r^{*-}) \sim -n \ln (r^* - r), \tag{6.9}$$

where r^* is found from (6.8) by using $\hat{\theta}_0 = \infty$ in the upper limit of the integral. This type of singularity, encountered previously in ignition studies (**9** to **11**, **14**, **18**) is indicative of the onset of a full-scale explosion. Thus we may conclude that when $\hat{a}_1 = -2{\cdot}3381$ the process involves a delayed supercritical reaction. The notion of delay is significant because in a normal supercritical event the explosion occurs when $\tau = O(1)$. Here, on the other hand, the rapid reaction takes place when $\tau = O(1/\epsilon)$.

In view of the fact that dramatically different processes take place near the stability boundary at $\hat{a}_1 \equiv \hat{a}_{11} = -2{\cdot}338\ldots$, it is useful to examine the solution $\phi_0(z)$ when

$$\hat{a}_1 = \hat{a}_{11} + \delta, \qquad 0 < \delta \ll 1. \tag{6.10}$$

If it is recalled that $A_1(\hat{a}_{11}) = 0$, then from (5.9a) (5.11), (6.10) and the Airy function properties (**17**) it can be shown that

$$\phi_0(z) = -\Gamma\left\{\frac{A_1'(z) + |\hat{K}|\ \delta B_1'(z)}{A_1(z) + |\hat{K}|\ \delta B_1(z)}\right\}, \qquad \hat{K} = \frac{A_1'(\hat{a}_{11})}{B_1(\hat{a}_{11})} < 0, \tag{6.11}$$

where $z > \hat{a}_1$. For finite z and $\delta \ll 1$

$$\phi_0(z) \approx -\Gamma A_1'(z)/A_1(z),$$

which represents a monotonically increasing function. However, for any specified $\delta \ll 1$, when $z \to \infty$ the exponential growth of the $B_1(z)$ prevails and

$$\phi_0(z) \approx -\Gamma z^{\frac{1}{2}}\{1 + O(z^{-\frac{3}{2}})\}. \tag{6.12}$$

Thus for any nonzero δ the temperature first rises, passes through a maximum and subsequently becomes large and negative.

The first zero of (6.11) for $\delta \ll 1$ is located near $z = z^* = -1{\cdot}01879$ where $A_1'(z^*) = 0$, while the second is found to be asymptotically far out, viz.

$$z^* \sim (-\tfrac{3}{4} \ln 2\,|\hat{K}|\ \delta)^{\frac{2}{3}}.$$

The location of the necessary positive maximum, $z = z_{\max}$, can be ascertained by examining the properties of $\phi'(z_{\max}) = 0$. In the limit $\delta \to 0$ one finds that

$$z_{\max} = \left\{\frac{A_1'(z_{\max})}{A_1(z_{\max})}\right\}^2.$$

These estimates indicate that for any non-zero δ there will come a time, however delayed, when the heat-loss effect is greater than the chemical heat production and hence the reaction is ultimately subcritical. This suggests that a more accurate evaluation of the critical value of a in (5.15) would result from a study of higher-order solution properties.

When $\hat{a}_1 < -2{\cdot}3381$ there exists a singularity at some finite value of $z = z_c$. The asymptotic form of $\phi_0(z)$ can be used to show that

$$T(s \to s_c^-) \sim 1 + \epsilon + \epsilon^{\frac{4}{3}}\{\Gamma/\hat{\gamma}(s_c - s) + \dots\}, \qquad (6.13)$$
$$y(s \to s_c^-) \sim 1 - \epsilon^{\frac{2}{3}}\{\gamma e s_c + o(1)\},$$

where s_c and z_c are related by (5.9d). These results suggest a non-uniformity when $s_c - s = O(\epsilon^{\frac{1}{3}})$. This occurs when $\tau_c - \tau = O(1)$ where $\tau_c = s_c/\epsilon^{\frac{1}{3}}$, $T = 1 + O(\epsilon)$ with $\Delta T = O(\epsilon)$, and $y = 1 + O(\epsilon^{\frac{2}{3}})$ but with $\Delta y = O(\epsilon)$. The fuel consumption estimate is rather different from the $O(1)$-variation found in the subcritical and critical cases. This is due to the fact that the supercritical behaviour occurs at a finite value of s (or z). Hence there is less time for fuel consumption to occur. The time-history solution in this time period and those subsequent to it will, in the interests of brevity, not be dealt with here. They are, however, quite similar to the fully supercritical solution described in detail in (**11**), with the exception that in the present work the explosion occurs when $\tau = O(\epsilon^{-\frac{1}{3}})$, compared to $\tau = O(1)$ in (**11**). The delay, once again, is caused by being very close to the stability boundary.

7. Conclusions

A detailed solution has been developed for several phases of the nearly critical spatially homogeneous model of a thermal explosion controlled by one-step irreversible kinetics. During the initiation phase, which takes place over a time period scaled by the conduction time, there is a gradual monotonic rise in temperature and decline in reactant concentration. This differs from solution behaviour in the supercritical case (**11**) where a full-blown explosion occurs at a finite value of the same time scale, and in the fully subcritical case (**8**) where the temperature actually begins to decline for large values of the time. In the subsequent time regime, $O(\epsilon^{-\frac{1}{3}})$ with respect to the conduction time, the temperature variation magnitude is smaller than during the initiation phase while the reactant variation is larger (e.g. see (4.1) and (5.1)). The temperature variation described by $\phi_0(s)$ is extremely sensitive to the value of heat loss parameter defined in (4.2). Thus it was found that for sufficiently small heat loss defined by $\hat{a}_1 < -2{\cdot}388\dots$ a rapid increase in temperature could be expected at a finite value in the s-plane. When $\hat{a}_1 = -2{\cdot}388\dots$ the character of the reaction changed radically in that there was gradual but relentless temperature growth with increasing time in the s-plane. And it was shown that over an even longer time scale, $O(\epsilon^{-1})$ with respect to the conduction time, a delayed full explosion would occur. Thus when $\hat{a}_1 \to -2{\cdot}388^-\dots$ the chemical heat release is very nearly balanced by the heat loss over a rather long $O(\epsilon^{-\frac{1}{3}})$-period of time. However over a sufficiently long time period, $O(\epsilon^{-1})$, the reaction overpowers the heat sink and a full rapid reaction occurs. A delayed thermal runaway process is observed to be characteristic of systems with near-critical heat loss! For all other values of heat loss corresponding to $a_1 > -2{\cdot}388$, an ultimate decline in the s-plane temperature is unavoidable. Hence over the longer time scale $O(\epsilon^{-1})$ with respect to the conduction time, it is implied that the reactant is completely consumed as the temperature falls gradually toward the initial value.

The results of this work, plus the related effort in (**9** to **11**) suggest quite definitively that the criticality criterion in the high activation energy model of the spatially homogeneous thermal explosion is to lowest order that predicted by classical studies (**8**, **14**). When a more accurate theory is used, like that developed here, which includes reactant consumption, then a finer definition of the criterion is obtained.

Finally, it may be noted that the one-dimensional model of a tubular reactor is described by the equations employed in the present analysis (**3**). Thus the results may be used to ascertain the thermal sensitivity of that device.

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